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N-type doping of poly(p-phenylene vinylene) with air-stable dopants

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The electron transport in poly(*p*-phenylene vinylene) (PPV) derivatives blended with the air-stable n-type dopant (4-(1,3-dimethyl-2,3-dihydro-1*H*-benzoimidazol-2-yl)phenyl)dimethylamine (N-DMBI) is investigated. This dopant is activated after thin film deposition by annealing and strongly enhances the electron transport due to filling of electron traps as well as donation of free electrons to the lowest unoccupied molecular orbital (LUMO) of PPV. As a result, the electron current in a doped device exceeds the trap-free hole current. The total generated free electron density in the LUMO by the dopant typically amounts to 10^{23} m^{-3}. © *2011 American Institute of Physics*.
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Organic semiconductors are a promising alternative to conventional opto-electronic semiconductors, because of their ease of processing, flexibility, and low cost. However, charge transport in organic semiconductors is governed by hopping conduction, leading to charge carrier mobilities and conductivities that are orders of magnitude lower as compared to their inorganic counterparts. One way to improve the conductivity and charge injection in organic semiconductors is through doping. Currently, a wide range of materials have been adopted as p-type dopant for organic semiconductors. However, effective n-type doping of solution-processed layers remains complicated. Many well-studied conjugated polymers, such as poly(*p*-phenylene vinylene) (PPV) derivatives, have their lowest unoccupied molecular orbital (LUMO) around 3.0 eV below the vacuum level. Therefore, n-type dopants are required to have an extremely shallow highest occupied molecular orbital (HOMO) (<3.0 eV), in order to allow electron transfer to the LUMO of the polymer. As a result of their low ionization potential, such n-type dopants are susceptible to air and moisture,[1] which requires that the devices are processed in inert atmosphere, which is not compatible with roll-to-roll production. As for vacuum deposited organic layers, most commonly used n-type dopants are alkali metals, such as Li (Ref. 2) and Cs,[3] or their salts.[4,5]

Recently, Wei *et al*. presented a n-type dopant, (4-(1,3-dimethyl-2,3-dihydro-1*H*-benzoimidazol-2-yl)phenyl)dimethylamine (N-DMBI),[6] of which the chemical structure is depicted in the inset of Figure 1. With N-DMBI as the n-type dopant, the conductivity of [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM) thin film transistors could be increased by several orders of magnitude and the negatively shifted threshold voltage was observed to scale with doping concentration. An important asset of N-DMBI is its stability under ambient conditions. By virtue of its relatively deep HOMO (4.6 eV), charge transfer between host and dopant molecules is energetically not favorable in the blend solution, preventing the formation of aggregates. The blend solution is therefore homogenous, transparent, and easy to process. However, since charge transfer from dopant to host does not occur, the dopant can be considered inactive. The dopant can be activated after film formation has completed, by means of a thermal annealing step. The N-DMBI molecules will release a hydrogen atom and become radicals. The singly occupied molecular orbital (SOMO) of the N-DMBI radical is located at 2.36 eV below vacuum, which is shallow enough to donate an electron to the LUMO of PPV. In this report, we demonstrate solution-processed layers of PPV doped with N-DMBI, for which the electron transport can be strongly increased in a diode configuration.

To investigate the influence of doping on the electron transport of the polymer, electron-only diodes were fabricated. In this study, two different polymers were used as active layers, poly(2-methoxy-5-(2'-ethyl-hexyloxy)-*p*-phenylene vinylene) (MEH-PPV) and poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO-PPV). These PPV derivatives have identical HOMO and LUMO levels and similar charge carrier mobilities that

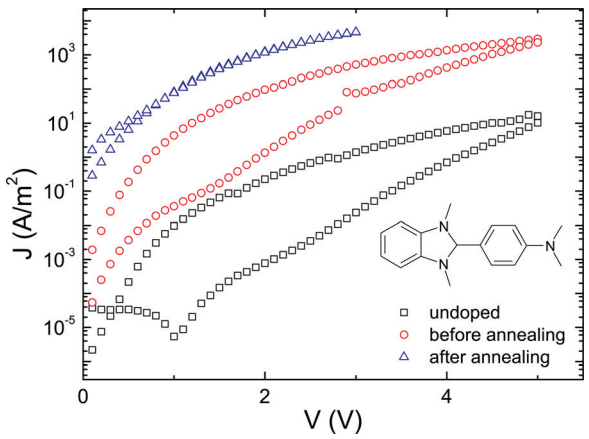

FIG. 1. (Color online) *J–V* characteristics of undoped and N-DMBI doped MDMO-PPV electron-only devices before and after annealing. The doping ratio is 20:1 (by wt.). The thickness of the undoped and doped devices are 75 nm and 160 nm, respectively. The inset shows the chemical structure of N-DMBI.

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slightly vary with the molecular weight of the polymer. N-DMBI was dissolved in chlorobenzene. MDMO-PPV and MEH-PPV were dissolved in toluene. The polymer and dopant were mixed in a 20:1 weight ratio. The undoped and doped MEH-PPV and MDMO-PPV layers were sandwiched between an Al(30 nm) anode and a Ba(5 nm)/Al(100 nm) cathode. The Al anode was oxidized by exposure to air to form a monolayer of Al_2O_3,[7] leading to a shift in work function from 4.2 eV to 3.7 eV and thereby increasing the hole-injection barrier to the HOMO of MEH-PPV or MDMO-PPV (5.3 eV). Fig. 1 shows the current density–voltage (J–V) characteristics of MDMO-PPV electron-only devices. A clear difference in electron transport between undoped and doped devices can be observed. The current density of a doped device after annealing is hysteresis-free and orders of magnitude higher than that of the undoped device. As frequently observed for electron-only devices, the first J–V sweep of the undoped device shows a strong irreversible hysteresis effect, which is ascribed to deeply trapped electrons in the polymer.[8–11] Surprisingly, even before annealing, the doped device exhibits a higher electron current and smaller hysteresis than the undoped device. The HOMO of N-DMBI is 4.6 eV, which is far below the LUMO of MDMO-PPV. A plausible explanation is that when dissolving N-DMBI in chlorobenzene, the solution was heated to 70 °C and subsequently cooled down to room temperature. Because the radical formation of N-DMBI molecules is a reversible process, most of the N-DMBI molecules will relax to their original states when cooling down. However, there might be a small amount of the dopant molecules staying in their radical states. Therefore, part of MDMO-PPV molecules may have been doped in the blend solution, which accounts for the enhancement of the current of a doped device before annealing. After annealing the devices at 65 °C for 30 min, a further improvement of the device current was measured, indicating that more N-DMBI molecules have converted to their radical states. The hysteresis disappeared completely, suggesting that most of the electron traps in the polymer are filled and free electrons are generated in the device. Similar behavior was observed in MEH-PPV electron-only devices.

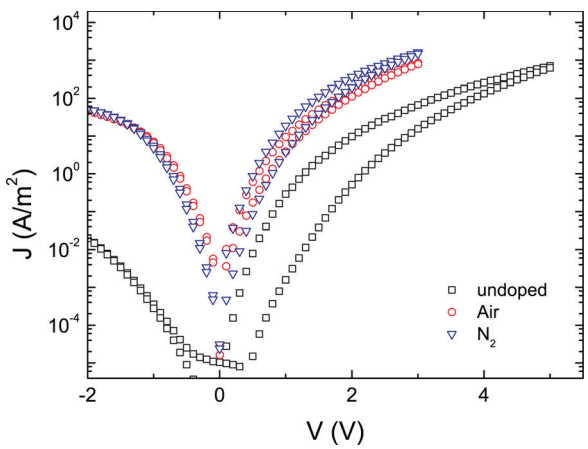

FIG. 2. (Color online) J–V characteristics of undoped (square) and N-DMBI doped MEH-PPV electron-only devices before annealing, with (circle) and without (triangle) dopant exposed to air. The doping ratio is 20:1 (by wt.). All devices have a layer thickness of 100 nm.

To avoid contamination with water and oxygen, all devices were fabricated and measured in a glove box under nitrogen atmosphere. To study the stability of N-DMBI, the dopant powder was exposed to ambient air for 30 min prior to preparation of the solutions. Compared to a normal N-DMBI doped MEH-PPV electron-only device, the device for which the dopant was exposed to air exhibits equal J–V characteristics, which confirms that N-DMBI is air stable (Fig. 2). Note that the reverse bias current of the undoped device is significantly lower than the forward bias current. Under reverse bias, the electron-injection is suppressed by the large injection barrier, which stems from the difference between the work function of Al/Al_2O_3 (3.7 eV) and the LUMO of MEH-PPV (2.9 eV). In contrast, the doped devices exhibit much higher currents under reverse bias voltage. This can be ascribed to the increased electron density in the film, which leads to band bending[12] and may induce charge dipoles on the Al_2O_3/polymer interface,[13,14] therefore reduces the injection barrier. Generally, in order to achieve Ohmic electron injection, low work function metals such as Ba and Ca are commonly used as cathode in state-of-the-art polymer light-emitting diodes (PLEDs). These metals are not air stable, which requires encapsulation in order to warrant long-term operation under ambient conditions. For N-DMBI doped charge-transport layers, these highly reactive metals are not required to achieve efficient charge injection, enabling the use of more stable electrodes. As a result, much longer device life-times are expected without sacrificing the device efficiency.[6]

To investigate whether the current in a doped electron-only device can surpass the trap-free space-charge limited current, hole-only devices with MEH-PPV sandwiched between a poly(3,4-ethylenedioxythiophene):poly(4-styrene sulphonate) (PEDOT:PSS) covered ITO anode and an Au cathode were fabricated. Fig. 3 shows a direct comparison of the electron current in undoped and doped MEH-PPV electron-only devices, with the corresponding hole current of a hole-only device of equal thickness. As reported by Chua *et al.*[15] for organic field-effect transistors and by Zhang *et al.*[16] for diodes, MEH-PPV has identical carrier mobilities

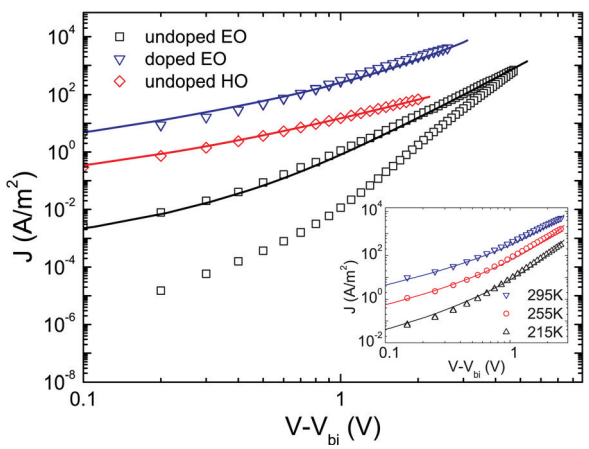

FIG. 3. (Color online) J–V characteristics of an undoped MEH-PPV hole-only (HO) device, an undoped electron-only (EO) device, and an N-DMBI doped electron-only device after annealing, with a doping ratio of 20:1 (by wt.). The inset shows the J–V characteristics of the doped EO device at different temperatures. All the devices have a layer thickness of 100 nm. The applied voltage was corrected for the built-in voltage (V_{bi}). The solid lines represent the numerical simulations.

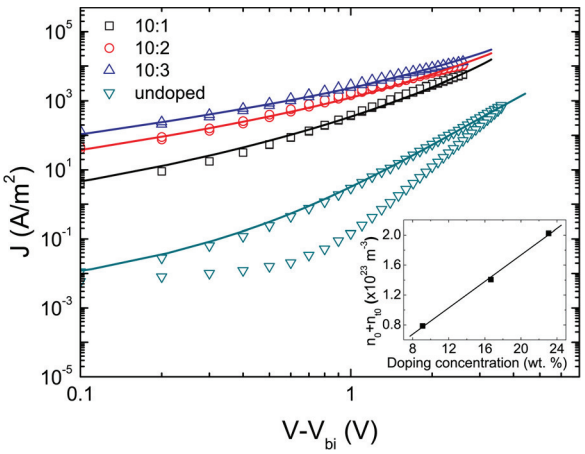

FIG. 4. (Color online) *J–V* characteristics of undoped and N-DMBI doped MEH-PPV electron-only devices with different weight ratios. All the devices have the same thickness: 80 nm. The applied voltage was corrected for the built-in voltage (V_{bi}). The solid lines represent the numerical simulations. The inset shows the amount of ionized dopants at zero bias $n_{t0}+n_0$ as a function of doping concentration.

for electrons and holes. However, electron currents are strongly trap-limited in MEH-PPV, whereas hole currents show a trap-free space-charge-limited behavior. Therefore, electron currents are substantially lower than the hole currents in this polymer. From Fig. 3, however, it is clear that after doping with N-DMBI, the electron current rises above the hole current. This suggests that the dopant not only fills all the traps but additionally generates free electrons in the LUMO of MEH-PPV, as expected from the shallow SOMO of the N-DMBI radical.

To gain more quantitative insight in the electron transport upon doping, we have analyzed the *J–V* characteristics with a numerical drift-diffusion model.[17] In this model, the charge carrier mobility depends on carrier density, electric field, and temperature.[18] From the numerical simulation, the estimated zero-field, low-density carrier mobility $\mu_0(T)$ at room temperature amounts to 5×10^{-11} m^2/Vs for electrons and holes, respectively. To describe the electron current, an exponential distribution of electron traps within the band gap is used.[19] To fully characterize the charge transport of doped devices, two more parameters are required: the total amount of electrons generated by the dopant at zero bias (n_0+n_{t0}) and the field-enhancement factor γ. n_0 and n_{t0} represent the density of free and trapped electrons, respectively. Under equilibrium conditions, the relation between n_0 and n_{t0} is given by

$$n_{t0} = N_t \cdot \left(\frac{n_0}{N_C}\right)^{\frac{T}{T_t}}, \tag{1}$$

with N_C the effective density of states, N_t the trap density and T_t the trap temperature. The field-assisted ionization of the dopant[20] is described by the Poole-Frenkel relation[21]

$$n_0(E) = n_0 \exp(\gamma\sqrt{E}). \tag{2}$$

By adding (n_0+n_{t0}) and γ to the model, the *J–V* characteristics of the doped electron-only devices at different temperatures can be fitted (inset of Fig. 3). The total number of electrons generated by the dopant (n_0+n_{t0}) is calculated to be in the order of $\sim10^{23}$ m^{-3}. Furthermore, the doping concentration was varied from 10:1, 10:2, and 10:3 (wt. %) and a linear dependence of (n_0+n_{t0}) on doping concentration was observed, see Fig. 4 and the inset of Fig. 4. The big advantage of this doping method is that it allows for wet deposition of n-type doped organic semiconductors in ambient atmosphere, opening a way to use these n-type doped layers in roll-to-roll processed devices. Besides increasing the conductivity, the concomitant effect of doping is that it reduces the injection barrier and allows electron injection from Al_2O_3 to the LUMO of the polymer, hence reactive metals can be replaced by non-reactive metals as the cathode.

In conclusion, we have presented solution-processed n-doped polymer diodes. When using the air-stable organic compound, N-DMBI, as the n-type dopant, the compatibility issue—the charge transfer between dopant and polymer molecules in solution—can be circumvented. After thermal activation, an enhancement of the electron current in the doped electron-only device is observed. From numerical simulations, we concluded that by doping, all the deep electron traps in MEH-PPV are filled and free charge carriers are generated in the device.

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